

WO 01/04187

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PCT/EP00/06161

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Preparations that are devoid of cross-linking agents

Field of the invention

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The invention is in the field of biopolymers and relates to crosslinker-free preparations obtained by precipitation and subsequent dewatering of biopolymers, and to a process for their preparation.

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Prior art

Japanese patent application JP-A1 Hei 6/048 917 (Nagawa) discloses beauty packagings containing chitosan as active component and organic acids and collagen as further constituents. Japanese patent application JP-A2 Hei 4/275 207 (Nitta Gelatin) relates to moisture-binding additives for skin cosmetic compositions which are pulverulent mixtures of chitosan and collagen.

20 European patent application EP A2 627 225 (Hüls) describes superabsorbents of chitosans reacted with acid which are present in the form of a powder.

German patent application DE-A1 196 43 066 (Henkel) discloses collagen-free cosmetic preparations which are prepared by crosslinking cationic biopolymers with diisocyanates and/or dialdehydes. US patent US 5,322,935 (Allied Signal Inc.) describes highly porous crosslinked bodies of nitrogen-containing polymers, and a process for their preparation. In this process, a nitrogen-containing polymer is firstly dissolved in water or an aqueous acid, then ionically crosslinked using an anionic salt solution in order, finally, to be covalently crosslinked by means of crosslinking agents.

35 The crosslinking agents mentioned here are, for example, dialdehydes and aromatic and aliphatic diisocyanates.

International application WO 96/20015 (Kimberly-Clark) describes water-swellaable, water-insoluble chitosan salts with a defined absorption capacity under the external application of pressure, which can be prepared by crosslinking. Japanese patent application JP-A2 03165775 (Katakura Chikkarin Co.) describes the preparation of N-succinyl-chitosans in the form of a multiporous sponge or film by crosslinking with hexamethylene diisocyanate. These sponges or films are suitable as prosthetic material for wound dressings, artificial blood vessels or hemostatic dressings. European patent EP-B1 663 212 (Hydromer Inc.) describes gels obtained by crosslinking chitosan with polyvinylpyrrolidone.

A common feature of all of the prior art products is that the bonding of the biopolymers is achieved by chemical crosslinking of reactive centers of the biopolymers. Bifunctional reagents are normally used for this purpose, such as, for example, dialdehydes or diisocyanates. Since the complete reaction of these chemical crosslinkers cannot usually be presupposed, residues of these crosslinkers remain in the product in certain circumstances. This may, particularly in preparations which remain on the skin for relatively long periods, such as cosmetic compositions or medicaments, in particular masks, or wound dressings, lead to irritations or allergies. This is a major disadvantage, particularly in the case of wound dressings which are applied to skin which is already irritated or damaged. Moreover, the addition of these chemical crosslinkers adversely affects biodegradability.

In addition, products crosslinked with the customary chemical crosslinkers cannot be used as foods or food supplements or as drug carriers for oral applications.

It was therefore the object of the present invention to provide crosslinker-free preparations which have properties comparable with known preparations prepared using crosslinkers. In particular, it should be possible
5 to prepare a three-dimensional structure, in the form of a block, a nonwoven material or a mask. Particular attention is paid in connection to properties such as mechanical stability in the dry and wet state, swellability and also compatibility with other possible
10 ingredients. Furthermore, the preparation should be simple and variable depending on the desired properties of the end-product. Biodegradability of the product is also desirable.

15 Description of the invention

5/10/02
The invention provides crosslinker-free preparations obtainable by adding precipitating agents to aqueous solutions and/or homogenized suspensions of biopolymers
20 and then dewatering the mixtures.

Surprisingly, it has been found that the preparations obtainable in this way have properties comparable with known crosslinker-containing preparations. In
25 particular, using the preparations according to the invention, it is possible to prepare three-dimensional structures, such as blocks, nonwoven materials or masks which are comparable with the products of the prior art as regards their mechanical stability, elasticity, their
30 swellability, water absorption capacity and their compatibility with other ingredients. The preparations according to the invention additionally have high skin compatibility and are biodegradable. Moreover, they can be prepared in a technically simple manner.

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The mechanical stability of the preparations according to the invention, measured as the tensile breaking

strength in accordance with DIN 53 571, test sample B, is in the range from 10 and 1 000 mN/mm², preferably in the range from 50 to 200 in the dry state and between 10 and 500, preferably between 30 and 100 mN/mm² in the wet state. The elasticity determined as elongation at break (method in accordance with DIN 53 571, test sample B) in % is between 1 and 50, in particular between 5 and 20% in the dry state.

The preparations according to the invention have a water absorption capacity of at least 5 g of water/g of product, in particular of at least 15 g of water/g of product. To determine the water absorption, the material is moistened with deionized water and weighed.

The present invention further provides a process for the preparation of crosslinker-free preparations in which precipitating agents are added to aqueous solutions and/or homogenized suspensions of biopolymers, and then the mixtures are dewatered.

In contrast to chemical crosslinking, the present process is based on the finding that the addition of precipitating agents leads to a shift in the pH, which results in partial or complete precipitation and simultaneously a physical crosslinking of the biopolymer. In contrast to chemical crosslinking, the crosslinking of the fibers here is not achieved by covalent bonds, but presumably on the basis of ion-pair formation, electrostatic attraction and mechanical twisting of the fibers.

For the purposes of the present application, crosslinker-free is thus to be understood as meaning that the mechanical stability of the preparation is achieved primarily by physical crosslinking, in particular that no chemical crosslinkers, such as bi- or

multifunctional reagents (for example dialdehydes or diisocyanates) are used for the crosslinking.

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Biopolymers

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For the purposes of the present application, the term "biopolymers" covers a group of naturally occurring macromolecules which are essential constituents of living organisms and are formed by polycondensation reactions. For the purposes of the present invention, it is possible, in principle, to use all biopolymers which are in the form of an aqueous solution or which can be prepared as aqueous suspensions and with which physical crosslinking takes place as a result of the addition of a precipitating agent.

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For the purposes of the present application, particularly suitable biopolymers are polysaccharides, such as, for example, inulin, mannans, galactans, xylans, chitin, chitosan, cellulose, pectins, alginates, carrageenes, agar-agar, carob seed grain and derivatives thereof, such as, for example, carboxymethylcelluloses, anionically or nonionically derivatized chitosans. A large number of these biopolymers carry carboxyl and/or sulfonyl groups, which gives them polyelectrolyte character. A differentiation can be made between anionic, nonionic and cationic biopolymers according to the overall charge of the biopolymers.

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30 Aqueous solutions and/or homogenized suspensions

The biopolymers are used as aqueous solutions and/or homogenized suspensions. The suspensions of the biopolymers usually contain dissolved fractions of the biopolymers. Cationic biopolymers are usually dissolved or suspended in aqueous mineral acids or aqueous organic carboxylic acids. Suitable mineral acids are

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hydrochloric acid, phosphoric acid, nitric acid and sulfuric acid, and organic carboxylic acids which may be mentioned are: formic acid, lactic acid, propionic acid, maleic acid, pyruvic acid, glycolic acid, succinic acid, acetic acid, citric acid, tartaric acid and adipic acid. Particular preference is given to hydrochloric acid, lactic acid and glycolic acid. Anionic biopolymers are usually dissolved or suspended in aqueous inorganic bases or aqueous organic nitrogen bases. Suitable inorganic bases are aqueous solutions of carbonates, hydrogencarbonates, hydrogenphosphates and hydroxides of alkali metal and alkaline earth metals, ammonia, and organic nitrogen bases, such as, for example, triethylamine or triethanolamine.

The amounts of solvent used are those which are required to partially or completely dissolve the biopolymers.

A 0.1 to 15% strength by weight aqueous solution or suspension with dissolved fractions of the biopolymers is normally used, preference being given to a 0.5 to 10% strength by weight, in particular a 1.0 to 5.0% by weight and in particular a 1.5 to 2.5% strength by weight, aqueous solution or suspension. Here, it has proven advantageous to adjust the concentration of the aqueous solution and/or suspension such that the solution or suspension has a viscosity in the range from 1 000 to 100 000 mPas (measured according to Brookfield, temperature of 20°C). In particular, a viscosity in the range from 10 000 to 40 000 mPas, preferably in the range from 15 000 to 35 000 mPas has proven advantageous. In the case of a suspension of the biopolymers, it may be advantageous to homogenize the suspension in order to achieve the desired viscosity. Suitable for this purpose are, in principle, all known methods of homogenization, e.g. colloid mills or gap homogenizers. The use of a colloid mill has proven

particularly advantageous for the preparation of an homogenized suspension. The homogenization is usually carried out at temperatures in the range from 0 to 100°C, in particular at 30 to 65°C.

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The aqueous solution or homogenized suspension of the biopolymers usually has a pH in the range from 1 to 12 depending on the nature of the biopolymer and the solvent used.

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Precipitating agents

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Suitable precipitating agents are, in principle all substances which shift the pH of the aqueous solution or homogenized suspension containing dissolved fractions of the biopolymers into the other pH range in each case and in so doing effect an at least partial precipitation and, as a consequence thereof, physical crosslinking of the biopolymers. To shift the pH from the alkaline into the acidic range, aqueous solutions of mineral acids or of organic carboxylic acids are suitable. Examples of suitable mineral acids are hydrochloric acid, phosphoric acid, nitric acid and sulfuric acid, and organic carboxylic acids which may be mentioned are: formic acid, lactic acid, propionic acid, maleic acid, pyruvic acid, glycolic acid, succinic acid, acetic acid, citric acid, tartaric acid and adipic acid. Particular preference is given to hydrochloric acid, lactic acid and glycolic acid. To shift the pH from the acidic into the alkaline range, aqueous inorganic bases or aqueous organic nitrogen bases are suitable. Suitable inorganic bases are aqueous solutions of carbonates, hydrogen carbonates, hydrogen phosphates and hydroxides of alkali metals and alkaline earth metals, ammonia, and examples of suitable organic nitrogen bases are triethylamine or triethanolamine. In a preferred embodiment, the inorganic base used is sodium hydrogencarbonate.

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The present invention encompasses the knowledge that the mechanical properties of the end-product can be influenced via the ratio of precipitating agent to solvent present: if complete precipitation of the biopolymer is desired, the amount of base or acid used is equimolar to the amount of acid or base, respectively, used (usually 0.8-1.2 mol of base:1 mol of acid, in particular 0.9-1.1 mol of base:1 mol of acid, and in particular 1 mol of base:1 mol of acid and vice versa). If the requirements for the mechanical properties of the end-product are lower, only a partial precipitation with less than the equimolar amount of base or acid can be carried out. If high alkalinity or acidity in the end-product is desired, a molar excess of base or acid, respectively, can be used.

As a result of the treatment with the precipitating agent, the pH of the aqueous solution or homogenized suspension of the biopolymers is usually adjusted to a pH of from 1 to 14, in particular to a pH of from 4.0 to 8.5, depending on the solution and precipitation system.

Dewatering

The present invention incorporates the knowledge that it is possible to influence the mechanical stability of the end-product through the choice of dewatering method and through the parameters of the method chosen in each case.

Suitable dewatering methods are, for example, air drying, vacuum drying, in particular at temperatures of from 20 to 100°C or above 100°C, and freeze-drying.

In a preferred embodiment of the present invention, freeze-drying is used for the dewatering.

It has proven particularly suitable to carry out a freezing step before the dewatering. This is advantageous particularly in the combination with freeze-drying. The present invention encompasses the knowledge that the structure produced as a result of the precipitation of the fibers, which is fixed by the freezing operation, is essentially retained during the dewatering in the form of freeze-drying. For this purpose, the suspension adjusted to the desired viscosity and mixed with precipitating agent is frozen at temperatures below the freezing point, with consideration of the desired geometric shape. The more rapid the freezing operation, the more finely pored and uniform the sponge which results after freeze-drying. Freezing can be carried out in customary freezing baths or else in chilling cabinets using liquefied gases, in particular liquid nitrogen, as the chilling medium. Intermediate storage of the frozen suspension up to a few days or weeks is possible in principle and has no disadvantageous effect on the quality of the end-product.

The freeze-drying is carried out in accordance with the prior art, as summarized, for example by G.-W. Oetjen in *Gefriertrocknen [Freeze-drying]*, Wiley-VCH Verlag, 1997, 1st Edition, Weinheim. It has proven advantageous to carry out the freeze-drying so that the frozen material does not thaw or start to thaw at any point in time at any place. For cost reasons, it has proven advantageous to speed up the drying operation by inputting energy, e.g. via radiant heat. To avoid discoloration, it is advantageous to increase the temperature in the already dried parts of the product no more than is necessary, so that product damage does not arise.

Preparation of the preparations

Usually, aqueous solutions or suspensions of the biopolymers with a dry substance content of from 0.1 to 15, preferably 0.5 to 10, in particular 1.0 to 5.0% by weight and particularly preferably 1.5 to 2.5% by weight are prepared at a pH of from 1.0 to 12, preferably 4.0 to 10 by adding inorganic or organic acids, preferably hydrochloric acid, glycolic acid and/or lactic acid or inorganic or organic bases, preferably sodium hydrogencarbonate or ammonia, where the temperature should be chosen so that it aids swelling of the biopolymers. This is usually in the range from 0 to 100°C and preferably 30 to 65°C. The suspensions prepared in this way also contain swollen undissolved particles in addition to the dissolved biopolymers. The viscosity of the suspension, established as a result of such conditions, can influence the subsequent mechanical properties of the nonwoven materials.

To improve the elasticity in the dry state, polyols and further auxiliaries and additives can be added to the suspensions. For the mechanical properties of the preparations, it has also proven advantageous to add natural fibers, such as, for example, lignin, polyose, pectin and, in particular, cellulose but also synthetic fibers, such as, for example, polyesters, polyamides or mixtures thereof in an amount of from 1 to 50% by weight, preferably 5 to 10% by weight, to the suspensions. In particular, it is advisable to add the fibers to the solution or to the suspension prior to homogenization. The suspensions are then homogenized. After the aqueous solutions and/or homogenized suspensions have been prepared in the desired viscosity range, they are usually degassed, e.g. by vacuum or ultrasound, to avoid the inclusion of gas bubbles.

The addition and homogeneous distribution of the precipitating agent can be carried out at a rate (usually 1 to 10, preferably 1 to 4, minutes) such that

precipitation and physical crosslinking of the biopolymer largely only takes place after chilling of the corresponding freeze mold. For the formation of the physical crosslinking, it has proven particularly advantageous to leave the product to stand without further mixing for 10 min to 10 hours, in particular 30 min to 6 h. The precipitating agent can be added by means of a mixing element with static and/or moving internals. The resulting suspension can be poured into a suitable mold corresponding to the geometric shape desired for the end-product. Depending on the desired shape of the end-product, these may be dishes, pipes, hoses, syringes etc. Varying layer thicknesses of the end-product can be established in freeze dishes via the fill level of the suspension. For the preparation of preparations in the form of nonwoven materials which are used, for example, as cosmetic agents or medicaments or medicinal products, the layer thicknesses are usually 1 to 100 mm, in particular from 15 to 35 mm.

A freezing phase then usually follows before the preparation is dewatered.

Further auxiliaries and additives can be added either before the precipitating agent is added or else together with the precipitating agent. Preference is given to adding the other auxiliaries and additives prior to the addition of the precipitating agent. Here, it is also advantageous to adjust the solutions or suspensions containing the other auxiliaries and additives to a viscosity in the range from 1 000 to 100 000, preferably in the range from 10 000 to 40 000 mPas, in particular in the range from 15 000 to 35 000 mPas, before the precipitating agent is added.

In a further embodiment of the invention, the crosslinker-free preparations are charged with

auxiliaries and additives after the dewatering. In this connection, cosmetic or pharmaceutical active ingredients or aroma substances are, for example, applied using special techniques to the ready, dry preparation after the freeze-drying. For this purpose, the active ingredient is dissolved in a suitable solvent and applied to the sponge resulting after the freeze-drying, which acts in this embodiment as a carrier material, and the solvent is then gently removed. Typical solvents are, for example supercritical CO₂ or nonpolar or polar organic solvents such as, for example, hexane, ethanol or isopropanol. The present invention encompasses the knowledge that, in a crosslinker-free preparation, auxiliaries and additives can be added either before or at the same time as the addition of the precipitating agent, or else after the dewatering.

Auxiliaries and additives

The auxiliaries and additives used may be substances which are compatible with the crosslinker-free preparations and have a positive influence on the physical properties of the preparations and/or impart additional functionalities to the preparations. Particularly preferred auxiliaries and additives are substances chosen from the group consisting of polyols, emulsifiers, fibers, dyes, perfume oils, aroma substances, cosmetic active ingredients, pharmaceutical active ingredients and food additives.

The preparations according to the invention may comprise, in minor amounts, as further auxiliaries and additives, oily substances, synthetic and natural hydrocarbons, waxes, cationic polymers, thickeners, silicone compounds, biogenic active ingredients, film formers, preservatives, solubilizers, structurants and

protection solutions (cryoprotectant agents = CPA), UV light protection factors and the like.

5 **Polyols**, which for the purposes of the invention, are suitable as additional constituents of the crosslinker-free preparations, preferably have 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are:

- glycerol;
- 10 • alkylene glycols, such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol, and polyethylene glycols with an average molecular weight of from 100 to 1 000 daltons;
- 15 • technical-grade oligoglycerol mixtures with an intrinsic degree of condensation of from 1.5 to 10, such as, for example technical-grade diglycerol mixtures with a diglycerol content of from 40 to 50% by weight;
- 20 • lower alcohol glucosides, in particular those having 1 to 8 carbon atoms in the alkyl radical, such as, for example, methyl and butyl glucoside;
- sugar alcohols having 5 to 12 carbon atoms, such as, for example, sorbitol or mannitol,
- 25 • sugars having 5 to 12 carbon atoms, such as, for example, glucose or sucrose;
- amino sugars, such as, for example, glucamine.

30 The polyols are usually used in amounts of from 0.1 to 20% by weight, preferably 1 to 10% by weight, based on the dry substance of the biopolymers, the use of glycerol and polyethylene glycols being preferred.

35 Suitable **emulsifiers** are, for example, nonionogenic surfactants from at least one of the following groups:

- (b1) addition products of from 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide onto

linear fatty alcohols having 8 to 22 carbon atoms, onto fatty acids having 12 to 22 carbon atoms and onto alkylphenols having 8 to 15 carbon atoms in the alkyl group;

5 (b2) $C_{12/18}$ -fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide onto glycerol;

(b3) glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids
10 having 6 to 22 carbon atoms, and ethylene oxide addition products thereof;

(b4) alkyl mono- and oligoglycosides having 8 to 22 carbon atoms in the alkyl radical, and ethoxylated analogs thereof;

15 (b5) addition products of from 15 to 60 mol of ethylene oxide onto castor oil and/or hydrogenated castor oil;

(b6) polyols and, in particular polyglycerol esters, such as, for example, polyglycerol polyricinoleate or polyglycerol poly-12-hydroxystearate. Also
20 suitable are mixtures of compounds from two or more of these classes of substance;

(b7) addition products of from 2 to 15 mol of ethylene oxide onto castor oil and/or hydrogenated castor
25 oil;

(b8) partial esters based on linear, branched, saturated or unsaturated $C_{12/22}$ -fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (e.g. sorbitol)
30 and polyglucosides (e.g. cellulose);

(b9) trialkyl phosphates;

(b10) wool wax alcohols;

(b11) polysiloxane-polyalkyl-polyether copolymers and
35 corresponding derivatives;

(b12) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol as in German patent

11 65 574 and/or mixed esters of fatty acids having 6 to 22 carbon atoms, methylglucose and polyols, preferably glycerol and (b13) polyalkylene glycols.

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The addition products of ethylene oxide and/or of propylene oxide onto fatty alcohols, fatty acids, alkylphenols, glycerol mono- and diesters, and sorbitan mono- and diesters of fatty acids or onto castor oil are known commercially available products. They are homolog mixtures whose average degree of alkoxylation corresponds to the ratio of the quantitative amounts of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C_{12/18}-fatty acid mono- and diesters of addition products of ethylene oxide onto glycerol are known from German patent 20 24 051 as refatting agents for cosmetic preparations.

C_{8/18}-Alkyl mono- and oligoglycosides, their preparation and their use as surface-active substances are known, for example, from US 3,839,318, US 3,707,535, US 3,547,828, DE-B 19 43 689, DE-B 20 36 472 and DE-A1 30 01 064 and EP-A 0 077 167. They are prepared, in particular, by reacting glucose or oligosaccharides with primary alcohols having 8 to 18 carbon atoms. With regard to the glycoside radical, both monoglycosides, in which one cyclic sugar radical is bonded glycosidically to the fatty alcohol, and also oligomeric glycosides with a degree of oligomerization up to, preferably, about 8 are suitable. The degree of oligomerization here is a statistical average value which is based on a homolog distribution customary for such technical-grade products.

35 The emulsifiers are usually used in amounts of from 0.1 to 20% by weight, preferably 1 to 10% by weight, based on the dry substance of the biopolymers.

Suitable **oil substances** are, for example, Guerbet alcohols based on fatty alcohols having 6 to 18, preferably 8 to 10, carbon atoms, esters of linear C₆-C₂₀-fatty acids with linear C₆-C₂₀-fatty alcohols, 5 esters of branched C₆-C₁₃-carboxylic acids with linear C₆-C₂₀-fatty alcohols, esters of linear C₆-C₁₈-fatty acids with branched alcohols, in particular 2-ethylhexanol, esters of linear and/or branched fatty acids with polyhydric alcohols (such as, for example, dimerdiol or 10 trimertriol) and/or Guerbet alcohols, triglycerides based on C₆-C₁₀-fatty acids, esters of C₆-C₂₂-fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, in particular benzoic acid, vegetable oils, branched primary alcohols, substituted 15 cyclohexanes, Guerbet carbonates, dialkyl ethers, silicone oils and/or aliphatic or naphthenic hydrocarbons.

Synthetic hydrocarbons which may be used are, for 20 example, hydrogenated polyisobutene (synthetic squalane), polyisobutene, polyethylene, polypropylene. **Natural hydrocarbons** which can be used are terpenes, such as, for example, squalene or squalane. The hydrocarbons are usually used in amounts of from 0.1 to 25 20% by weight, preferably 1 to 10% by weight, based on the dry substance of the biopolymers.

Suitable **thickeners** are, for example, polysaccharides, in particular xanthan gum, guar-guar, agar-agar, 30 alginates and tyloses, carboxymethylcellulose and hydroxyethylcellulose, and also relatively high molecular weight polyethylene glycol mono- and diesters of fatty acids, polyacrylates, polyvinyl alcohol and polyvinylpyrrolidone.

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Suitable **cationic polymers** are, for example, cationic cellulose derivatives, cationic starch, copolymers of

diallylammonium salts and acrylamides, quaternized vinylpyrrolidone/vinylimidazole polymers, such as, for example, Luviquat® (BASF AG, Ludwigshafen/FRG), condensation products of polyglycols and amines,

5 quaternized collagen polypeptides, such as, for example, lauryldimonium hydroxypropyl hydrolyzed collagen (Lamequat®L, Grünau GmbH), quaternized wheat polypeptides, polyethylenimine, cationic silicone polymers, such as, for example, amidomethicones or Dow

10 Corning, Dow Corning Co./US, copolymers of adipic acid and dimethylaminohydroxypropyldiethylenetriamine (Cartaretine®, Sandoz/CH), polyaminopolyamides as described, for example, in FR-A 22 52 840, and crosslinked water-soluble polymers thereof, cationic

15 chitin derivatives, such as, for example, quaternized chitosan, optionally microcrystalline distributed, condensation products of dihaloalkylene, such as, for example, dibromobutane with bisdialkylamines, such as, for example, bisdimethylamino-1,3-propane, cationic guar

20 gum, such as, for example, Jaguar® CBS, Jaguar® C-17, Jaguar® C-16 from Celanese/US, quaternized ammonium salt polymers, such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 from Miranol/US.

25 Suitable **silicone compounds** are, for example, dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, and amino-, fatty-acid-, alcohol-, polyether-, epoxy-, fluorine- and/or alkyl-modified silicone compounds, which can either be liquid or in

30 resin form at room temperature.

Biogenic active ingredients are understood as meaning, for example, bisabolol, allantoin, phytantriol, panthenol, AHA acids, plant extracts, marine extracts, vitamins and vitamin complexes.

35 **Film formers** are, for example, chitosan, microcrystalline chitosan, quaternized chitosan,

polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof, and similar compounds.

5 **Dyes** which can be used are the substances approved and suitable for cosmetic purposes, as listed, for example, in the publication "Kosmetische Färbemittel" [Cosmetic colorants] from the Farbstoffkommission der Deutschen Forschungsgemeinschaft [Dyes Commission of the German
10 Research Society], Verlag Chemie, Weinheim, 1984, pp. 81-106. These dyes are usually used in concentrations of from 0.001 to 1% by weight, based on the dry substance of the biopolymers.

15 **Fibers** which can be used are either natural fibers or synthetic fibers, and mixtures thereof. Suitable natural fibers are, for example, lignin, polyose, pectin and, in particular, cellulose, and suitable synthetic fibers are, for example, polyesters, polyamides or mixtures
20 thereof. The fibers are preferably used in an amount of from 1 to 50% by weight, preferably 5 to 10% by weight.

Waxes are to be understood as meaning natural or synthetic substances which, at 20°C, are kneadable,
25 solid to brittly hard, coarse to finely crystalline, transparent to opaque, but not glasslike, melt above 40°C without decomposing, and are of low viscosity and not stringy even slightly above the melting point. The waxes to be used for the purposes of the invention
30 differ from resins, for example, by virtue of the fact that they usually convert into the molten, low-viscosity state between about 50 and 90°C, in exceptional cases also up to 200°C, and are virtually free from ash-forming compounds. Waxes are divided into the following
35 three groups depending on their origin: **natural waxes**, such as, for example, candelilla wax, carnauba wax, Japan wax, espartograss wax, cork wax, guaruma wax, rice

germ oil wax, sugarcane wax, ouricury wax, montan wax, beeswax, shellac wax, spermaceti wax, lanolin (wool wax), uropygial grease, ceresin, ozokerite (earth wax), petrolatum, paraffin waxes, microcrystalline waxes; 5 **chemically modified waxes** (hard waxes), such as, for example, montan ester waxes, sasol waxes, hydrogenated jojoba waxes, and **synthetic waxes**, such as, for example, polyalkylene waxes and polyethylene glycol waxes. In this connection, the use of natural waxes, specifically 10 of plant waxes, is preferable.

Aroma substances are concentrated preparations of fragrances or flavors which are intended to give foods a particular odor or taste. Examples are vanillin, 15 peppermint oil, Maillard products, banana flavoring and many others.

Important aroma substance carriers are the essential oils, and also mixtures of individual components of these oils, which are generally prepared synthetically, 20 the term "nature-identical" being used in this connection. There are currently approximately 600 natural aroma substances and approximately 4 200 nature-identical aroma substances for foods, cosmetic compositions and pharmaceutical products. **Perfume oils** 25 which may be mentioned are, for example, mixtures of natural and synthetic odorants. Natural odorants are extracts from flowers, stems and leaves, fruits, fruit peels, roots, woods, herbs and grasses, needles and branches, and resins and balsams. Also suitable are 30 animal raw materials, such as, for example, civet and castoreum. Typical synthetic odorant compounds are products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Odorant compounds of the ester type are, for example, benzyl acetate, p-tert-butylcyclohexyl acetate, linalyl acetate, phenylethyl 35 acetate, linalyl benzoate, benzylformate, allyl cyclohexylpropionate, styrallyl propionate and benzyl

salicylate. The ethers include, for example, benzyl ethyl ether, and the aldehydes include, for example, the linear alkanals having 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen
5 aldehyde, hydroxycitronellal, lilial and bourgeonal, the ketones include, for example, the ionones and methyl cedryl ketone, the alcohols include anethole, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and terpineol, and the hydrocarbons
10 include mainly the terpenes and balsams. However, preference is given to using mixtures of different odorants which together produce a pleasing scent note. Essential oils of relatively low volatility, which are mostly used as aroma components, are also suitable as
15 perfume oils, e.g. sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olibanum oil, galbanum oil, labdanum oil and lavandin oil. Preference is given to using bergamot oil, dihydromyrcenol, lilial,
20 lyral, citronellol, phenylethyl alcohol, α -hexylcinnamaldehyde, geraniol, benzylacetone, cyclamen aldehyde, linalool, boisambrene forte, ambroxan, indole, hedione, sandelice, lemon oil, mandarin oil, orange oil, allyl amyl glycolate, cyclovertal, lavandin oil, clary
25 sage oil, β -damascone, geranium oil bourbon, cyclohexyl salicylate, vertofix coeur, iso-E-super, fixolide NP, evernyl, iraldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romilat, irotyl and floramat alone or in mixtures.

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Food additives are understood as being substances with or without nutritional value which are usually neither themselves consumed as foods, nor used as characteristic food additives and are added to a food for technological
35 reasons during the manufacture, processing, preparation, treatment, packaging, transportation or storage; as a result of which they themselves or their secondary

products are or can become constituents of the food. Some food additives are natural in origin, such as, for example, the carotene from carrots, chlorophyll from green plants, lecithin from eggs or soybeans. Others, by contrast, are purely synthetic chemicals, such as, for example, the azo dyes tartrazine and amaranth, the antioxidants BHA and BHT and the sweeteners saccharin and cyclamate.

10 **Pharmaceutical active ingredients** covers active ingredients and therapeutic substances and carriers thereof in the various medicament forms. Examples which may be mentioned are azelaic acid as antiacne agent or PVP-iodine complex for disinfection.

15 **Cosmetic active ingredients** which can be used are all substances which are suitable for use in cosmetic compositions.

20 **Suitable preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid, and the other classes of substances listed in Annex 6, Parts A and B of the Cosmetics Directive.

25 **UV light protection factors** are understood as meaning, for example, organic substances (light protection filters) which are in liquid or crystalline state at room temperature and which are able to absorb ultraviolet rays and release the absorbed energy again in the form of longer-wave radiation, e.g. heat. UVB filters may be oil-soluble or water-soluble. Examples of oil-soluble substances are:

35 **> 3-benzylidenecamphor or 3-benzylidenenorcamphor and derivatives thereof, e.g. 3-(4-methylbenzylidene)-camphor as described in EP 0693471 B1;**

- 4-aminobenzoic acid derivatives, preferably 2-ethylhexyl 4-(dimethylamino)benzoate, 2-octyl 4-(dimethylamino)benzoate and amyl 4-(dimethylamino)benzoate;
- 5 ➤ esters of cinnamic acid, preferably 2-ethylhexyl 4-methoxycinnamate, propyl 4-methoxycinnamate, isoamyl 4-methoxycinnamate, 2-ethylhexyl 2-cyano-3,3-phenylcinnamate (octocrylene);
- 10 ➤ esters of salicylic acid, preferably 2-ethylhexyl salicylate, 4-isopropylbenzyl salicylate, homomenthyl salicylate;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- 15 ➤ esters of benzalmalonic acid, preferably di-2-ethylhexyl 4-methoxybenzmalonate;
- triazine derivatives, such as, for example, 2,4,6-trianilino(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and Octyl Triazone, as described in
- 20 **EP 0818450 A1** or Dioctyl Butamido Triazone (Uvasorb® HEB);
- propane-1,3-diones, such as, for example, 1-(4-tert-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dione;
- ketotricyclo(5.2.1.0)decane derivatives, as described
- 25 in **EP 0694521 B1**.

Suitable water-soluble substances are:

- 30 ➤ 2-phenylbenzimidazole-5-sulfonic acid and the alkali metal, alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and its salts;
- 35 ➤ sulfonic acid derivatives of 3-benzylidenecamphor, such as, for example 4-(2-oxo-3-bornylidenemethyl)-

benzenesulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)sulfonic acid and salts thereof.

Suitable typical UV-A filters are, in particular,
5 derivatives of benzoylmethane, such as, for example,
1-(4'-tert-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-
dione, 4-tert-butyl-4'-methoxydibenzoylmethane (Parsol
1789), 1-phenyl-3-(4'-isopropylphenyl)propane-1,3-dione
and enamine compounds as described in DE 19712033 A1
10 (BASF). The UV-A and UV-B filters can of course also be
used in mixtures. In addition to said soluble
substances, insoluble light protection pigments, namely
finely disperse metal oxides or salts, are also suitable
for this purpose. Examples of suitable metal oxides are,
15 in particular, zinc oxide and titanium dioxide and also
oxides of iron, zirconium, silicon, manganese, aluminum
and cerium, and mixtures thereof. Salts which can be
used are silicates (talc), barium sulfate or zinc
stearate. The oxides and salts are used in the form of
20 pigments for skin care and skin-protecting emulsions and
decorative cosmetics. The particles here should have an
average diameter of less than 100 nm, preferably between
5 and 50 nm, and in particular between 15 and 30 nm.
They can have a spherical shape, although it is also
25 possible to use those particles which have an
ellipsoidal shape or shape which differs in another way
from the spherical form. The pigments can also be
surface-treated, i.e. be present in hydrophilicized or
hydrophobicized form. Typical examples are coated
30 titanium dioxides, such as, for example, Titandioxid T
805 (Degussa) or Eusolex® T2000 (Merck). Suitable
hydrophobic coating agents here are primarily silicones
and, specifically, trialkoxyoctylsilanes or
simethicones. In sunscreen compositions, micropigments
35 or nanopigments are preferably used. Preference is given
to using micronized zinc oxide. Further suitable UV

light protection filters are given in the overview by P. Finkel in SÖFW-Journal 122, 543 (1996).

In addition to the two abovementioned groups of primary
5 light protection substances, it is also possible to use
secondary light protection agents of the antioxidant
type, which break the photochemical reaction chain which
is triggered when UV radiation penetrates the skin.
Typical examples thereof are amino acids (e.g. glycine,
10 histidine, tyrosine, tryptophan) and derivatives
thereof, imidazoles (e.g. urocanic acid) and derivatives
thereof, peptides, such as D,L-carnosine, D-carnosine,
L-carnosine and derivatives thereof (e.g. anserine),
carotenoids, carotenes (e.g. α -carotene, β -carotene,
15 lycopene) and derivatives thereof, chlorogenic acid and
derivatives thereof, lipoic acid and derivatives thereof
(e.g. dihydrolipoic acid), aurothioglucose,
propylthiouracil and other thiols (e.g. thioredoxin,
glutathione, cysteine, cystine, cystamine and the
20 glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl
and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl
and glyceryl esters thereof), and salts thereof,
dilauryl thiodipropionate, distearyl thiodipropionate,
thiodipropionic acid and derivatives thereof (esters,
25 ethers, peptides, lipids, nucleotides, nucleosides and
salts), and sulfoximine compounds (e.g. buthionine
sulfoximines, homocysteine sulfoximine, buthionine
sulfones, penta-, hexa-, heptathionine sulfoximine) in
very low tolerated doses (e.g. pmol to μ mol/kg), also
30 (metal) chelating agents (e.g. α -hydroxy fatty acids,
palmitic acid, phytic acid, lactoferrin), α -hydroxy
acids (e.g. citric acid, lactic acid, malic acid), humic
acid, bile acid, bile extracts, bilirubin, biliverdin,
EDTA, EGTA and derivatives thereof, unsaturated fatty
35 acids and derivatives thereof (e.g. γ -linolenic acid,
linoleic acid, oleic acid), folic acid and derivatives
thereof, ubiquinone and ubiquinol and derivatives

thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (vitamin A palmitate), and
5 coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α -glycosylrutin, ferulic acid, furfurylidene-glucitol, carnosine, butylhydroxytoluene, butylhydroxyanisole, nordihydroguaiacic acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric
10 acid and derivatives thereof, mannose and derivatives thereof, superoxide dismutase, zinc and derivatives thereof (e.g. ZnO, ZnSO₄), selenium and derivatives thereof (e.g. selenomethionine), stilbenes and derivatives thereof (e.g. stilbene oxide, trans-stilbene
15 oxide) and the derivatives (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of said active ingredients which are suitable according to the invention.

20 **Cryoprotectant agents** are, for example, sugar solutions, such as sucrose, maltose and the like, glycerol, PVP and also buffer solutions.

The total amount of auxiliaries and additives may be 0.1
25 to 50% by weight, preferably 0.5 to 10% by weight, based on the dry substance of the biopolymers.

Industrial applicability

30 The preparations according to the invention are characterized by high skin compatibility and high fluid absorption capacity. The present invention therefore further relates to the use of the preparations according to the invention as cosmetic agents, in particular as
35 dry films, absorbers, and cosmetic masks and hemostatic sponges for small cut wounds, e.g. caused by a razor.

The invention further relates to the use of the preparations according to the invention as medicaments and/or medicinal products, in particular as wound tampons, wound dressings, burn wound dressings, 5 dressings which release an active ingredient, nonwoven materials and as drug carriers for oral applications. In this connection, the preparations according to the invention can be charged with a variety of topical pharmaceutical formulations. For oral applications, the 10 preparations according to the invention can serve, for example, as carrier e.g. for antibiotics, analgesics and others.

The invention further provides for the use of the 15 preparations according to the invention as foods. Here, foods is to be understood as meaning all substances which are intended for human consumption in the unchanged, prepared or processed state. These include, in particular, food supplements and diet foods. The 20 preparations according to the invention are, moreover, suitable for use as food additives.